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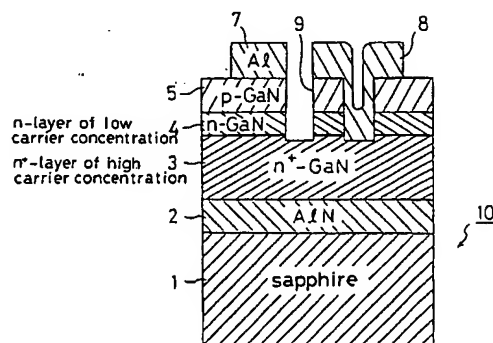
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(54) Light emitting semiconductor device using gallium nitride group compound.

(57) There are disclosed two types of gallium nitride LED having the pn junction. An LED of gallium nitride compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ ) comprises an n-layer; a p-layer which exhibits p-type conduction upon doping with p-type impurities and irradiation with electron rays, the p-layer joining to the n-layer; a first electrode for the n-layer so as to join to the n-layer, passing through a hole formed in the p-layer which extends from the p-layer to the n-layer; and a second electrode for the p-layer which is formed in a region which is separated by a groove formed in the p-layer so as to extend from the upper surface of the p-layer to said n-layer. An LED comprises an n-layer; an i-layer doped with p-type impurities, the i-layer joining to the n-layer; a first electrode for said n-layer so as to join to the n-layer, passing through a hole formed in the i-layer which extends from the upper surface of the i-layer to the n-layer; a p-type part in a specific region in the i-layer which is converted into p-type conduction by irradiating with electron rays, the p-type part being formed such that said first electrode is in-

sulated and separated by the i-layer; and a second electrode for said p-type part.

FIG.1.



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## BACKGROUND OF THE INVENTION

### 1. Field of the Invention:

The present invention relates to a light-emitting semiconductor device using gallium nitride group compound which emits a light in the region from blue to ultraviolet, and also to a process for producing the same.

### 2. Description of the Prior Art:

It is known that GaN compound semiconductor can be made into a light-emitting semiconductor device, such as a light-emitting diode (LED), which emits a blue light.

The GaN compound semiconductor attracts attention because of its high light-emitting efficiency resulting from a direct transition and of its ability to emit a blue light which is one of the three primary colors.

The light-emitting diode of GaN compound semiconductor is composed of a sapphire substrate, an n-layer and an i-layer grown thereon. The n-layer of the GaN compound semiconductor with n-type conduction is directly grown on the surface of the sapphire substrate or grown on a buffer layer of aluminum nitride formed on the sapphire substrate. The i-layer of semi-insulating (i-type) GaN compound semiconductor is doped with p-type impurities. (See Japanese Patent Laid-open Nos. 119196/1987 and 188977/1988.)

The voltage for driving this light-emitting diode, however, is high. Consequently, there is room for improvement.

Another disadvantage of the gallium nitride compound semiconductor is that it does not become p-type but remains i-type (semi-insulator) even though it is doped with p-type impurities.

As the results of extensive studies, the present inventors succeeded in producing a p-type gallium nitride compound semiconductor. This led to the creation of a pn junction that emits a blue light efficiently.

The light-emitting diode comprising the pn junction, however, presents a problem associated with insulating the electrode for a lower layer from an upper layer in case that the electrode for the lower layer is formed through the upper layer to get the electrode on the upper layer, because the p-layer and n-layer are electrically conductive.

## SUMMARY OF THE INVENTION

The present invention was completed to solve this problem. It is an object of the present invention to provide a light-emitting semiconductor device using gallium nitride group compound which has a

new pn junction and a new structure for leading the electrodes. This light-emitting device operates at a lower voltage.

According to an embodiment of the present invention, the pn junction is made of gallium nitride compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ ) and the electrodes for the p-layer and n-layer are led from either p-layer or n-layer, whichever upper.

The p-layer of gallium nitride compound semiconductor is formed in the following manner. First, gallium nitride compound semiconductor is formed by a vapor phase epitaxy. During the vapor phase epitaxy, the gallium nitride compound semiconductor is doped with p-type impurities to form a semi-insulating i-layer. The i-layer is irradiated with electron rays to form the p-layer of p-type semiconductor. The p-layer is joined with the n-layer to form the pn junction. The respective electrodes for the p-layer and n-layer are formed on the upper layer. The electrode for the lower layer is connected through a hole made in the upper layer.

The upper layer has a groove formed therein which electrically insulates and separates the hole and the electrode for the lower layer formed through the hole. The electrode for the upper layer is formed in the region separated by the groove and opposite to the other electrode.

The p-layer is doped with, for example, magnesium (Mg). Simple doping gives rise to an i-type (insulating) semiconductor, and the i-type layer changes into the p-layer upon irradiation with electron rays. This irradiation is carried out at an acceleration voltage of 1 Kv to 50 Kv and a sample current of  $0.1 \mu\text{A}$  to 1 mA.

Because of the pn junction realized for the first time by the present inventors, it is possible to lower the operating voltage and to improve the light-emitting efficiency and the light intensity.

In addition, with the groove formed in the upper layer, it is possible to electrically insulate and separate the upper layer from the electrode for the lower layer.

The above-mentioned structure makes it possible to produce a light-emitting device having the pn junction and the bump connection (with face down) formed for both electrodes on the upper layer.

According to another embodiment of the present invention, a p-layer of gallium nitride compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ ) is formed on an n-layer, and part of the i-layer is converted into p-type, so that a partial pn junction is formed, and the electrodes for both layers are led from the upper i-layer. This structure is produced in the following manner.

First, an n-layer is formed from an n-type gallium nitride compound semiconductor. An i-layer of gallium nitride compound semiconductor doped with p-type impurities is formed on the n-layer.

Upon doping with the p-type impurities, the gallium nitride compound semiconductor becomes an insulator although it does not change into p-type.

The electrode for the n-layer is formed on the surface of the i-layer through a hole formed in the i-layer so that the hole reaches the n-layer. A p-type part is formed on the specific region of the i-layer so that the electrode for the n-layer is insulated and separated by the i-layer. The p-type part is formed by irradiating the specific region of the i-layer with electron rays. In other words, the i-type (insulating) gallium nitride compound semiconductor decreases in resistance upon irradiation with electron rays, changing into a p-type semiconductor. The thus converted p-layer and the lower n-layer form the pn junction. An electrode for the p-type part is formed on this p-type part.

Thus the electrode for the lower n-layer is insulated and separated from the p-type part by the i-layer.

The i-layer is doped with, for example, magnesium (Mg). The irradiation is carried out at an acceleration voltage of 1 kV to 50 kV and a sample current of 0.1  $\mu$ A to 1 mA.

Because of the pn junction realized for the first time by the present inventors as mentioned above, it is possible to lower the operating voltage.

As mentioned above, the electrode for the lower n-layer is insulated and isolated from the p-layer by the i-layer. This structure makes it possible to produce a light-emitting device having the bump connection (with face down) formed for both electrodes on the upper p-layer and i-layer.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic representation showing a structure of a light-emitting diode according to a first embodiment of the present invention.

Figs. 2 to 7 are sectional views showing the process of producing the light-emitting diode according to a first embodiment of the present invention.

Figs. 8A and 8B are graphs showing measured V-I characteristics of the pn type LED described in Example 1 and a MIS type LED, respectively.

Fig. 9 is a sectional view showing a structure of a light-emitting diode according to a second embodiment of the present invention.

Figs. 10 to 16 are sectional views showing the process of producing the light-emitting diode according to a second embodiment of the present invention.

Figs. 17A and 17B are graphs showing measured V-I characteristics of the pn type LED described in Example 2 and a MIS type LED, respectively.

Fig. 18 is a sectional view showing a structure of a light-emitting diode according to a third embodiment of the present invention.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention will be described in more detail with reference to the following examples.

##### Example 1

A light-emitting diode 10 as shown in Fig. 1 is composed of a sapphire substrate 1 and several layers formed thereon which include a 500 Å thick buffer layer 2 of AlN, a 2.2  $\mu$ m thick n<sup>+</sup>-layer 3 of GaN with a high carrier concentration, a 1.5  $\mu$ m thick n-layer 4 of GaN with a low carrier concentration and a 0.2  $\mu$ m thick p-layer 5 of GaN. An electrode 7 of aluminum is in contact with the p-layer 5, and an electrode 8 of aluminum is in contact with the n<sup>+</sup>-layer 3. The electrodes 7 and 8 separated from each other by a groove 9.

The light-emitting diode 10 of the above-mentioned structure was produced by the metalorganic vapor phase epitaxy (MOVPE) in the following manner. This process employed NH<sub>3</sub>, H<sub>2</sub> (carrier gas), trimethyl gallium Ga(CH<sub>3</sub>)<sub>3</sub> (TMG), trimethyl aluminum Al(CH<sub>3</sub>)<sub>3</sub> (TMA), silane SiH<sub>4</sub>, and cyclopentadienyl magnesium Mg(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (CP<sub>2</sub>Mg).

The process started with cleaning the single crystal sapphire substrate by washing with an organic solvent and by heat treatment. The cleaned sapphire substrate 1 whose principal surface was a-surface {11 $\bar{2}$ 0} was placed on the susceptor mounted in a reaction chamber of an MOVPE apparatus. The sapphire substrate 1 underwent vapor phase etching at 1100 °C with hydrogen flowing through the reaction chamber at a rate of 2 liters/min under normal pressure. The reaction chamber in which the temperature was lowered at 400 °C was supplied with H<sub>2</sub> at a flow rate of 20 liters/min, NH<sub>3</sub> at a flow rate of 10 liters/min, and TMA at a flow rate of 1.8 x 10<sup>-5</sup> mol/min, so as to form the 500 Å thick buffer layer 2 of AlN.

With the sapphire substrate 1 kept, at 1150 °C the reaction chamber was supplied with H<sub>2</sub> at a flow rate of 20 liters/min, NH<sub>3</sub> at a flow rate of 10 liters/min, TMG at a flow rate of 1.7 x 10<sup>-4</sup> mol/min, and silane SiH<sub>4</sub> (diluted to 0.86 ppm with H<sub>2</sub>) at a flow rate of 200 ml/min for 30 minutes, so as to form the 2.2  $\mu$ m thick n<sup>+</sup>-layer 3 of GaN with a high carrier concentration (1.5 x 10<sup>18</sup>/cm<sup>3</sup>).

With the sapphire substrate 1 kept at 1150 °C, the reaction chamber was supplied with H<sub>2</sub> at a flow rate of 20 liters/min, NH<sub>3</sub> at a flow rate of 10 liters/min, and TMG at a flow rate of 1.7 x 10<sup>-4</sup>

mol/min for 20 minutes, so as to form the 1.5  $\mu\text{m}$  thick n-layer 4 of GaN with a low carrier concentration ( $1 \times 10^{15}/\text{cm}^3$ ).

With the sapphire substrate 1 kept at 900 °C, the reaction chamber was supplied with  $\text{H}_2$  at a flow rate of 20 liters/min,  $\text{NH}_3$  at a flow rate of 10 liters/min, TMG at a flow rate of  $1.7 \times 10^{-4}$  mol/min, and  $\text{CP}_2\text{Mg}$  at a flow rate of  $3 \times 10^{-6}$  mol/min for 3 minutes, so as to form the 0.2  $\mu\text{m}$  thick i-layer 5 of GaN. The i-layer 5 as such is an insulator.

The i-layer 5 was uniformly irradiated with electron rays using a reflection electron diffraction apparatus. The conditions for irradiation are as follows: Acceleration voltage: 10 kV, sample currents 1  $\mu\text{A}$ , beam moving rate: 0.2 mm/sec, beam diameter: 60  $\mu\text{m}$ , and vacuum:  $2.1 \times 10^{-5}$  Torr. This irradiation changed the i-layer 5 which was an insulator having a resistivity greater than  $10^8 \Omega\text{cm}$  into a conducting semiconductor having a resistivity of 40  $\Omega\text{cm}$ . In this way, there was obtained the p-layer 5 which exhibits the p-type electric conduction.

The wafer of multi-layered structure as shown in Fig. 2 was got by the above-mentioned steps. This wafer had many same elements which would be separated from one another later to make many chips. Figs. 3 to 7 are sectional views of a single device formed on the wafer.

A 2000 Å thick  $\text{SiO}_2$  layer 11 was formed on the p-layer 5 by sputtering as shown in Fig. 3. The  $\text{SiO}_2$  layer 11 was coated with a photoresist 12. The photoresist layer 12 was removed at positions A and B by photolithography. The position A is where a hole 15 is to be formed which reaches the n<sup>+</sup>-layer 3 of high carrier concentration. (In the hole 15 is formed later an electrode.) The position B is where a groove 9 is to be formed which separates said electrode forming part from the electrode for the p-layer 5.

The exposed parts of the  $\text{SiO}_2$  layer 11 which are not covered by the photoresist 12 were removed by etching with hydrofluoric acid, as shown in Fig. 4.

The exposed parts of the p-layer 5 and n-layer 4 of low carrier (which are not covered by the photoresist 12 and  $\text{SiO}_2$  layer 11) underwent dry etching with  $\text{CCl}_2\text{F}_2$  with Ar at a flow rate of 10 ml/min at 0.04 Torr and at a high-frequency power, 0.44 W/cm<sup>2</sup> and thereafter successively underwent dry etching as shown in Fig. 5. This dry etching was carried out till the upper surface of the n<sup>+</sup>-layer 3 was partly removed. A hole 15 for the electrode leading to the n<sup>+</sup>-layer 3 and a groove 9 for insulation and separation were formed by this step.

The  $\text{SiO}_2$  layer 11 remaining on the p-layer 5 was removed by etching with hydrofluoric acid, as shown in Fig. 6.

The upper surface of the sample was entirely covered with an Al layer 13 by vapor deposition, as shown in Fig. 7. The Al layer 13 was electrically connected to the n<sup>+</sup>-layer 3 through the hole 15.

The Al layer 13 was coated with a photoresist 14, which was subsequently patterned by photolithography so that the electrode leading to the n<sup>+</sup>-layer 3 and p-layer 5 remained.

The exposed part of the Al layer 13 not covered with the photoresist 14 underwent etching with nitric acid, with the photoresist 14 as a mask, as shown in Fig. 7. This etching completely removed the Al layer 13 formed by deposition on the inside of the groove 9. The photoresist 14 was removed with acetone. There remained the electrode 8 for the n<sup>+</sup>-layer 3 and the electrode for the p-layer 5.

After the above-mentioned steps, the wafer was cut into individual chips. Thus there was obtained a gallium nitride light-emitting diode having the pn junction structure, as shown in Fig. 1.

The voltage-current (V-I) characteristics of the light-emitting diode (pn junction type LED) 10 produced as mentioned above was measured. The result is shown in Fig. 8A. On the contrary the V-I characteristics of a conventional MIS (metal insulator semiconductor) type LED having an n-layer and a semi-insulating i-layer was measured. The result is shown in Fig. 8B. From the Figs. 8A and 8B it is known that the drive voltage at a drive current of 10 mA is about 8 volts in the pn junction type LED and the drive voltage is about 13 volts in the MIS type LED. Accordingly, the drive voltage is lower in the pn junction type LED than in the MIS type LED. From many measurements for many samples of the pn and MIS type LED's it was observed that the drive voltages of the pn type LED's little fluctuate but the drive voltages concerning the MIS type LED's fluctuate from 10 V to 15 V.

The magnesium doping gas used in the above-mentioned embodiment may be replaced by methylcyclopentadienyl magnesium  $\text{Mg}(\text{C}_5\text{H}_5)\text{-CH}_3$ .

In the above-mentioned embodiment, the n-layer is of double-layer structure composed of the n<sup>+</sup>-layer 3 of high carrier concentration and the n-layer 4 of low carrier concentration. However, these two layers may be replaced by a single n-layer.

In the case of the double-layer structure, the n-layer 4 of low carrier concentration should preferably have a carrier concentration of  $1 \times 10^{14}$  to  $1 \times 10^{17}/\text{cm}^3$  and a thickness of 0.5 to 2  $\mu\text{m}$ . With a carrier concentration higher than  $1 \times 10^{17}/\text{cm}^3$ , the light-emitting diode decreases in light intensity. With a carrier concentration lower than  $1 \times 10^{14}/\text{cm}^3$ , the light-emitting diode radiates heat be-

cause of the increased serial resistance. With a thickness greater than 2  $\mu\text{m}$ , the light-emitting diode radiates heat because of the increased serial resistance. With a thickness smaller than 0.5  $\mu\text{m}$ , the light-emitting diode decreases in light intensity.

In addition, the  $n^+$ -layer 3 should preferably have a carrier concentration of  $1 \times 10^{17}$  to  $1 \times 10^{19}/\text{cm}^3$  and a thickness of 2 to 10  $\mu\text{m}$ . A carrier concentration higher than  $1 \times 10^{19}/\text{cm}^3$  is not desirable because crystal property becomes poor. With a carrier concentration lower than  $1 \times 10^{17}/\text{cm}^3$ , the light-emitting diode radiates heat because of the increased serial resistance. A layer thickness greater than 10  $\mu\text{m}$  would cause the substrate to warp. With a layer thickness smaller than 2  $\mu\text{m}$ , the light-emitting diode radiates heat because of the increased serial resistance.

#### Example 2

A light-emitting diode 10 as shown in Fig. 9 is composed of a sapphire substrate 1 and several layers formed thereon which include a 500 Å thick buffer layer 2 of AlN, a 2.2  $\mu\text{m}$  thick  $n^+$ -layer 3 of GaN with a high carrier concentration, a 1.5  $\mu\text{m}$  thick  $n$ -layer 4 of GaN with a low carrier concentration, a 0.2  $\mu\text{m}$  thick  $i$ -layer 50 of GaN, and a  $p$ -layer 5 which exhibits the  $p$ -type electric conduction. The  $p$ -layer 5 is formed in a part of the  $i$ -layer 50.

There is a hole 15 which passes through the  $i$ -layer 50 and the  $n$ -layer 4 of low carrier concentration, reaching the  $n^+$ -layer 3 of high carrier concentration. There is an electrode 52 of aluminum which is formed on the  $i$ -layer 50 and is connected to the  $n^+$ -layer 3 of high carrier concentration through the hole 15. On the  $p$ -layer 5 is formed an electrode 51 of aluminum for the  $p$ -layer 5. The electrode 52 for the  $n^+$ -layer 3 of high carrier concentration is insulated and separated from the  $p$ -layer 5 by the  $i$ -layer 50.

The light-emitting diode 10 of the above-mentioned structure was produced by MOVPE in the following manner. This process employed  $\text{NH}_3$ ,  $\text{H}_2$  (carrier gas), TMG, TMA, silane  $\text{SiH}_4$ , and  $\text{CP}_2\text{Mg}$ .

The following steps gave rise to a wafer of multi-layered structure as shown in Fig. 9. This wafer was processed into a multiplicity of elements which were separated from one another later. Figs. 10 to 16 are sectional views of a single device formed on the wafer.

The process started with cleaning a single-crystal sapphire substrate by washing with an organic solvent and by heat treatment. The cleaned sapphire substrate 1 (whose  $a$ -plane is the principal surface) was placed on the susceptor mounted in the reaction chamber of the MOVPE apparatus. The sapphire substrate 1 underwent vapor phase

etching at 1100°C with hydrogen flowing through the reaction chamber at a rate of 2 liters/min under normal pressure. The reaction chamber in which the temperature was lowered at 400°C was supplied with  $\text{H}_2$  at a flow rate of 20 liters/min,  $\text{NH}_3$  at a flow rate of 10 liters/min, and TMA at a flow rate of  $1.8 \times 10^{-5}$  mol/min, so as to form a 500 Å thick buffer layer 2 of AlN.

With the sapphire substrate 1 kept at 1150°C, the reaction chamber was supplied with  $\text{H}_2$  at a flow rate of 20 liters/min,  $\text{NH}_3$  at a flow rate of 10 liters/min, TMG at a flow rate of  $1.7 \times 10^{-4}$  mol/min, and silane  $\text{SiH}_4$  (diluted to 0.86 ppm with  $\text{H}_2$ ) at a flow rate of 200 ml/min for 30 minutes, so as to form a 2.2  $\mu\text{m}$  thick  $n^+$  layer 3 of GaN with a high carrier concentration ( $1.5 \times 10^{18}/\text{cm}^3$ ).

With the sapphire substrate 1 kept at 1150°C, the reaction chamber was supplied with  $\text{H}_2$  at a flow rate of 20 liters/min,  $\text{NH}_3$  at a flow rate of 10 liters/min, and TMG at a flow rate of  $1.7 \times 10^{-4}$  mol/min for 20 minutes, so as to form a 1.5  $\mu\text{m}$  thick  $n$ -layer 4 of GaN with a low carrier concentration ( $1 \times 10^{15}/\text{cm}^3$ ).

With the sapphire substrate 1 kept at 900°C, the reaction chamber was supplied with  $\text{H}_2$  at a flow rate of 20 liters/min,  $\text{NH}_3$  at a flow rate of 10 liters/min, TMG at a flow rate of  $1.7 \times 10^{-4}$  mol/min, and  $\text{CP}_2\text{Mg}$  at a flow rate of  $3 \times 10^{-6}$  mol/min for 3 minutes, so as to form a 0.2  $\mu\text{m}$  thick  $i$ -layer 50 of GaN. The  $i$ -layer 50 as such was an insulator.

On the  $i$ -layer 50 was formed an  $\text{SiO}_2$  layer 11 (2000 Å thick) by sputtering, as shown in Fig. 11. The  $\text{SiO}_2$  layer 11 was coated with a photoresist 12. The photoresist at position A was removed by photolithography, where a hole 15 was to be formed later which passed through the  $i$ -layer 50 and the  $n$ -layer 4. The exposed part of the  $\text{SiO}_2$  layer 11 (which was not covered by the photoresist 12) was removed by etching with hydrofluoric acid, as shown in Fig. 12.

The exposed parts of the  $i$ -layer 50 and  $n$ -layer 4 (which are not covered by the photoresist 12 and the  $\text{SiO}_2$  layer 11) underwent dry etching with  $\text{CCl}_2\text{F}_2$  at a flow rate of 10 ml/min at 0.04 Torr and 0.44 W/cm<sup>2</sup> (high-frequency power) and thereafter successively dry etching with Ar. This dry etching was carried out till the surface of the  $n^+$ -layer 3 was etched. A hole 15 for the electrode leading to the  $n^+$ -layer 3 was formed by this step, as shown in Fig. 13.

The  $\text{SiO}_2$  layer 11 remaining on the  $i$ -layer 50 was removed by etching with hydrofluoric acid, as shown in Fig. 14.

The  $i$ -layer 50 was locally irradiated with electron rays using a reflection electron diffraction apparatus to form a  $p$ -type part 5 which was  $p$ -type semiconductor, as shown in Fig. 15. The conditions

for irradiation were as follows: Acceleration voltage: 10 kV, sample current: 1  $\mu$ A, beam moving rate: 0.2 mm/sec, beam diameter: 60  $\mu$ m $\phi$ , and vacuum:  $2.1 \times 10^{-5}$  Torr. This irradiation changed the i-layer 50 (which was an insulator having a resistivity greater than  $10^8 \Omega$ cm) into a p-type semiconductor having a resistivity of 35  $\Omega$ cm. The part other than the p-type part 5 (i.e., the part which was not irradiated with electron rays) remained the i-layer 50 which was an insulator. Therefore, the p-type part 5 formed the pn junction with the n-layer 4 in the vertical direction; but it was electrically isolated and insulated from its surrounding by the i-layer 50 in the horizontal direction.

An Al layer 20 was formed to cover the p-type part 5, the i-layer 50, and the inside of the hole 15, as shown in Fig. 16. The Al layer 20 was coated with a photoresist layer 21, which was to be subsequently patterned by photolithography so that electrodes for the n-layer 3 and the p-type part 5 remained unetched.

The exposed part of the Al layer 20 underwent etching with nitric acid, with the photoresist 21 as a mask. The photoresist 21 was removed with acetone. In this way there were formed the electrode 52 for the n-layer 3 and the electrode 51 for the p-type part 5, as shown in Fig. 9. After the above-mentioned steps, the wafer was cut into individual elements.

The V-I characteristics of the light-emitting diode (pn junction type LED) 10 produced as mentioned above was measured as well as in the example 1. The result is shown in Fig. 17A. The V-I characteristics of a conventional MIS type LED having an n-layer and a semi-insulating i-layer is shown in Fig. 17B. From the Figs. 17A and 17B it is known that the drive voltage at a drive current of 10 mA is about 8 volts in the pn junction type LED and the drive voltage is about 13 volts in the MIS type LED. Accordingly, the drive voltage is lower in the pn junction type LED than in the MIS type LED. From many measurements for many samples of the pn and MIS type LED's it was observed that the drive voltages of the pn type LED's little fluctuate but the drive voltages concerning the MIS type LED's fluctuate from 10 V to 15 V.

The magnesium doping gas used in the above-mentioned embodiment may be replaced by methylcyclopentadienyl magnesium Mg ( $C_5H_5$ )- $CH_3$ .

#### Example 3

A light-emitting diode 10 as shown in Fig. 18 is composed of a sapphire substrate 1 and several layers formed thereon which include a 500 Å thick buffer layer 2 of AlN, a 0.2  $\mu$ m thick p-layer 5 of GaN, a 1.5  $\mu$ m thick n-layer 4 of GaN with a low

carrier concentration and a 2.2  $\mu$ m thick n-layer 3 of GaN with a high carrier concentration. An electrode 8 of aluminum is in contact with the n-layer 3, and an electrode 7 of aluminum is in contact with the p-layer 5. The electrodes 7 and 8 separated from each other by a groove 9.

The light-emitting diode 10 of the above-mentioned structure was produced by the metalorganic vapor phase epitaxy (MOVPE) in the same manner as the example 1.

In the example 3, the order of forming the p-layer 5, the n-layer 4 and the n-layer 3 is only different from the example 1.

In the above-mentioned embodiment, the n-layer is of double-layer structure composed of an n-layer 3 of high carrier concentration and an n-layer 4 of low carrier concentration. However, these two layers may be replaced by a single n-layer.

In the case of double-layer structure, the n-layer should preferably have a carrier concentration of  $1 \times 10^{14}$  to  $1 \times 10^{17}/\text{cm}^3$  and a thickness of 0.5 to 2  $\mu$ m. With a carrier concentration higher than  $1 \times 10^{17}/\text{cm}^3$ , the light-emitting diode decreases in light intensity. With a carrier concentration lower than  $1 \times 10^{14}/\text{cm}^3$ , the light-emitting diode radiates heat because of the increased serial resistance. With a thickness greater than 2  $\mu$ m, the light-emitting diode radiates heat because of the increased serial resistance. With a thickness smaller than 0.5  $\mu$ m, the light-emitting diode decreases in light intensity.

In addition, the n-layer 3 should preferably have a carrier concentration of  $1 \times 10^{17}$  to  $1 \times 10^{19}/\text{cm}^3$  and a thickness of 2 to 10  $\mu$ m. A carrier concentration higher than  $1 \times 10^{19}/\text{cm}^3$  is not desirable because crystal property becomes poor. With a carrier concentration lower than  $1 \times 10^{17}/\text{cm}^3$ , the light-emitting diode radiates heat because of the increased serial resistance. A layer thickness greater than 10  $\mu$ m would cause the substrate to warp. With a layer thickness smaller than 2  $\mu$ m, the light-emitting diode radiates heat because of the increased serial resistance.

There are disclosed two types of gallium nitride LED having the pn junction. An LED of gallium nitride compound semiconductor ( $Al_xGa_{1-x}N$ , where  $0 \leq x < 1$ ) comprises an n-layer; a p layer which exhibits p-type conduction upon doping with p-type impurities and irradiation with electron rays, the p-layer joining to the n-layer; a first electrode for the n-layer so as to join to the n-layer, passing through a hole formed in the p-layer which extends from the p-layer to the n-layer; and a second electrode for the p-layer which is formed in a region which is separated by a groove formed in the p-layer so as to extend from the upper surface of the p-layer to said n-layer. An LED comprises an n-layer; an i-layer doped with p-type impurities, the i-layer join-

ing to the n-layer; a first electrode for said n-layer so as to join to the n-layer, passing through a hole formed in the i-layer which extends from the upper surface of the i-layer to the n-layer; a p-type part in a specific region in the i-layer which is converted into p-type conduction by irradiating with electron rays, the p-type part being formed such that said first electrode is insulated and separated by the i-layer; and a second electrode for said p-type part.

#### Claims

1. A light-emitting semiconductor device using gallium nitride group compound comprising:
  - an n-layer of n-type gallium nitride group compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ ); and
  - a p-layer of gallium nitride group compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ ) which exhibits the p-type conduction upon doping with p-type impurities and irradiation with electron rays, said p-layer joining to said n-layer.
2. A process for producing a light-emitting semiconductor device using gallium nitride group compound comprising the steps of:
  - forming an n-layer of n-type gallium nitride group compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ );
  - forming an i-layer of semi-insulator of gallium nitride group compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ ) doped with p-type impurities; and
  - converting said i-layer into a p-layer which exhibits p-type conduction by irradiating said i-layer with electron rays.
3. A light-emitting semiconductor device using gallium nitride group compound comprising:
  - an n-layer of n-type gallium nitride group compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ );
  - a p-layer of gallium nitride group compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ ) which exhibits the p-type conduction upon doping with p-type impurities and irradiation with electron rays, said p-layer joining to said n-layer;
  - a first electrode for said n-layer which is formed on an upper surface of said p-layer so as to join to said n-layer, passing through a hole formed in said p-layer which extends from said upper surface of said p-layer to said n-layer; and
  - a second electrode for said p-layer which is formed in a region opposite to said first electrode, said region being on said upper

surface of said p-layer and being separated from said first electrode by a groove formed in said p-layer so as to extend from said upper surface of said p-layer to said n-layer.

4. A light-emitting semiconductor device using gallium nitride group compound comprising:
  - an n-layer of n-type gallium nitride group compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ );
  - a p-layer of gallium nitride group compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ ) which exhibits the p-type conduction upon doping with p-type impurities and irradiation with electron rays;
  - an n-layer of n-type gallium nitride group compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ ), said n-layer joining to said p-layer;
  - a first electrode for said p-layer which is formed on an upper surface of said n-layer so as to join to said p-layer, passing through a hole formed in said n-layer which extends from said upper surface of said n-layer to said p-layer; and
  - a second electrode for said n-layer which is formed in a region opposite to said first electrode, said region being on said upper surface of said n-layer and being separated from said first electrode by a groove formed in said n-layer so as to extend from said upper surface of said n-layer to said p-layer.
5. A process for producing a light-emitting semiconductor device using gallium nitride group compound comprising the steps of:
  - forming an i-layer of semi-insulator of gallium nitride group compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ ) doped with p-type impurities on an n-layer of n-type gallium nitride group compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ );
  - converting said i-layer into a p-layer which exhibits p-type conduction by irradiating said i-layer with electron rays;
  - forming in said p-layer a hole extending from an upper surface of said p-layer to said n-layer in which an electrode for said n-layer is to be formed and also forming in said p-layer a groove which separates said hole;
  - forming on said p-layer surrounding said hole an electrode for said n-layer which passes through said hole to join to said n-layer; and
  - forming on said upper surface of said p-layer separated by said groove an electrode for said p-layer.

6. A process for producing a light-emitting semiconductor device using gallium nitride group compound comprising:

forming an i-layer semi-insulator of gallium nitride compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ ) doped with p-type impurities;

converting said i-layer into a p-layer which exhibits p-type conduction by irradiating said i-layer with electron rays;

forming on said p-layer an n-layer of gallium nitride group compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ );

forming in said n-layer a hole extending from an upper surface of said n-layer to said p-layer in which an electrode for said p-layer is to be formed and also forming in said n-layer a groove which separates said hole;

forming on said n-layer surrounding said hole an electrode for said p-layer which passes through said hole to join to said p-layer; and

forming on said upper surface of said n-layer separated by said groove an electrode for said n-layer.

7. A light-emitting semiconductor device using gallium nitride group compound comprising:

an n-layer of n-type gallium nitride group compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ );

an i-layer of semi-insulator or of gallium nitride group compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ ) doped with p-type impurities, said i-layer joining to said n-layer;

a first electrode for said n-layer which is formed on an upper surface of said i-layer so as to join to said n-layer, passing through a hole formed in said i-layer which extends from said upper surface of said i-layer to said n-layer;

a p-type part in a specific region in said i-layer which is converted into p-type conduction by irradiation with electron rays, said p-type part being formed such that said first electrode is insulated and separated from said p-type part by said i-layer; and

a second electrode for said p-type part which is formed on an upper surface of said p-type part.

8. A process for producing a light-emitting semiconductor device using gallium nitride group compound comprising:

forming an i-layer of semi-insulator of gallium nitride group compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ ) doped with p-type impurities on an n-layer of n-type gallium nitride group compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ );

forming in said i-layer a hole extending from an upper surface of said i-layer to said n-layer in which an electrode for said n-layer is to be formed;

forming a p-type part in a specific region in said i-layer which is converted into p-type conduction by irradiating with electron rays, said p-type part being formed such that said hole is separated from said p-type part by said i-layer;

forming on said i-layer surrounding said hole an electrode for said n-layer which passes through said hole to join to said n-layer; and

forming on an upper surface of said p-type part an electrode for said p-type part.

9. A light-emitting device according to Claim 3, wherein said n-layer is of double-layer structure composed of an n-layer of low carrier concentration in which the electron density is low and an  $n^+$ -layer of high carrier concentration in which the electron density is high, with the former layer joining to said p-layer, and said first electrode joins to said  $n^+$ -layer of high carrier concentration.

10. A light-emitting device according to Claim 4, wherein said n-layer is of double-layer structure composed of an n-layer of low carrier concentration in which the electron density is low and an  $n^+$ -layer of high carrier concentration in which the electron density is high, with the former layer joining to said p-layer, and said second electrode is formed on said  $n^+$ -layer of high carrier concentration.

11. A light-emitting device according to Claim 7, wherein said n-layer is of double-layer structure composed of an n-layer of low carrier concentration in which the electron density is low and an  $n^+$ -layer of high carrier concentration in which the electron density is high, with the former layer joining to said p-layer, and said first electrode joins to said  $n^+$ -layer of high carrier concentration.

12. A light-emitting device according to Claim 9, which further comprises a sapphire substrate and a buffer layer of aluminum nitride (AlN) formed thereon, with said  $n^+$ -layer of high carrier concentration being formed on said buffer layer.

13. A light-emitting device according to Claim 11, which further comprises a sapphire substrate and a buffer layer of aluminum nitride (AlN)



formed thereon, with said n<sup>+</sup>-layer of high carrier concentration being formed on said buffer layer.

14. A light-emitting device according to Claim 1, wherein irradiation with electron rays is carried out at an acceleration voltage of 1 kV to 50 kV and a sample current of 0.1  $\mu$ A to 1 mA.

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FIG.1

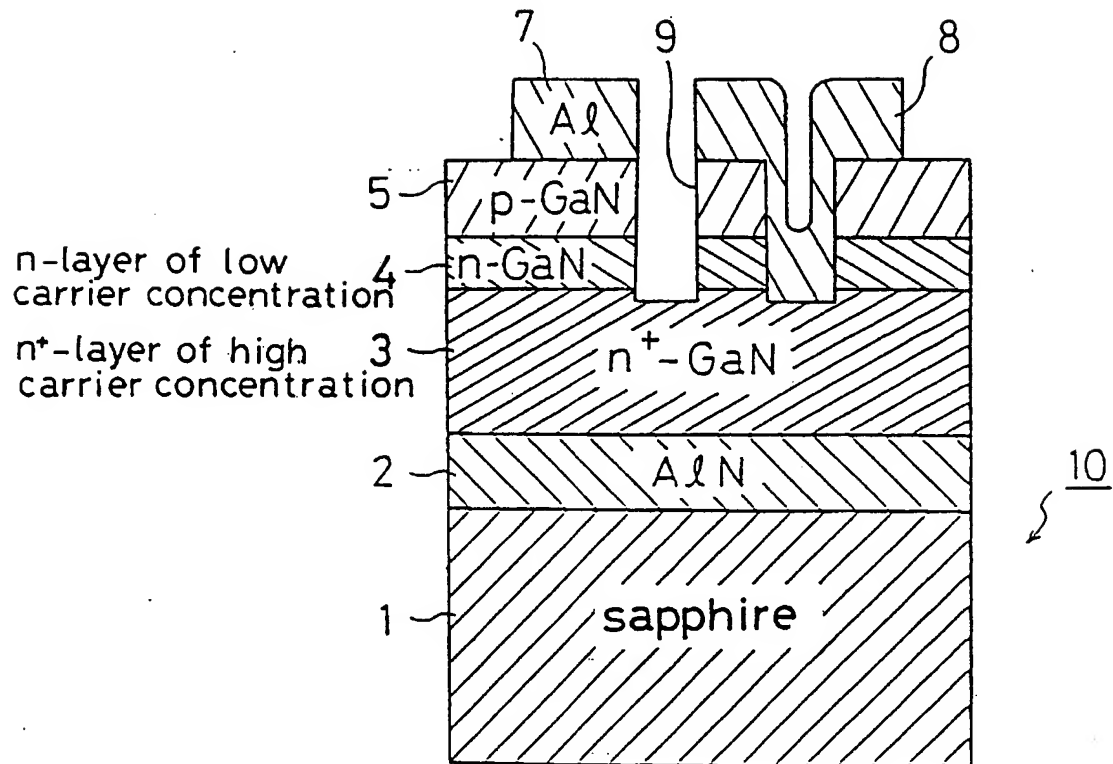


FIG. 2

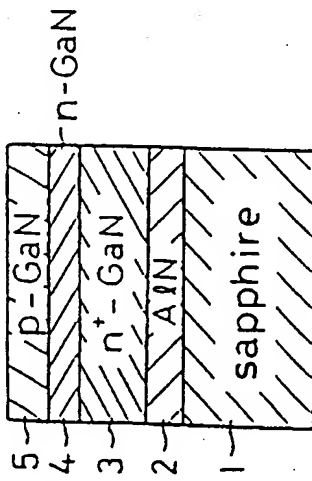


FIG. 3

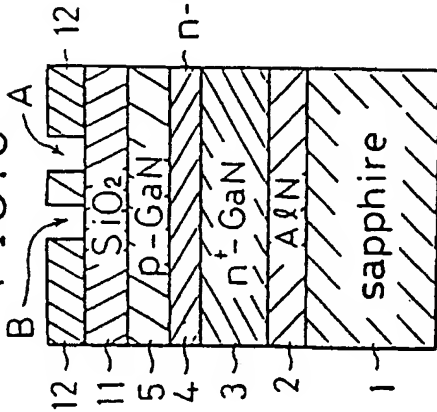


FIG. 4

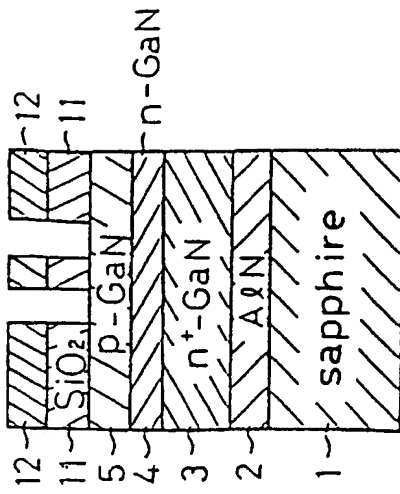


FIG. 5

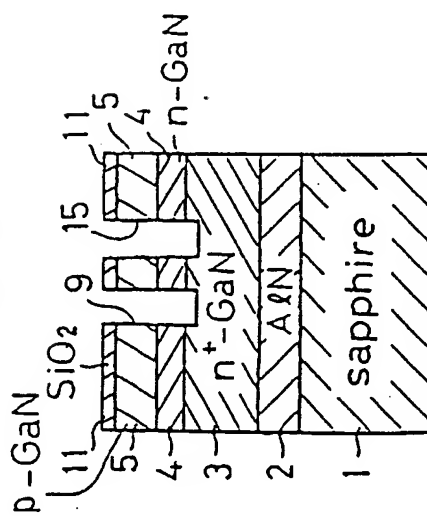


FIG. 6

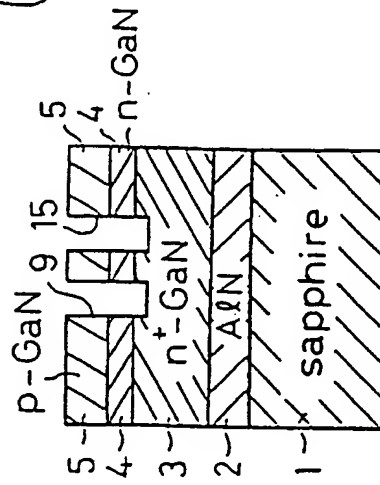


FIG. 7

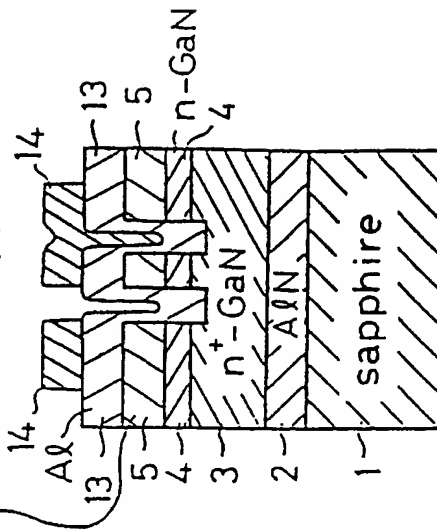


FIG. 8A

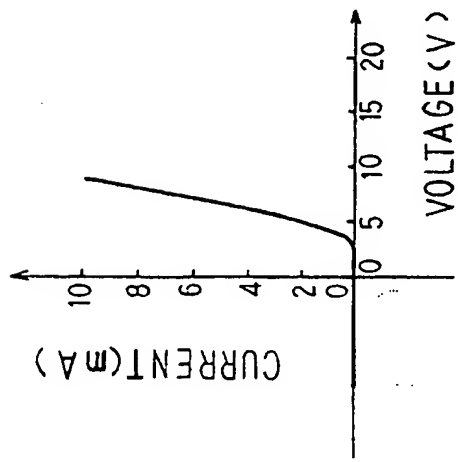


FIG. 8B

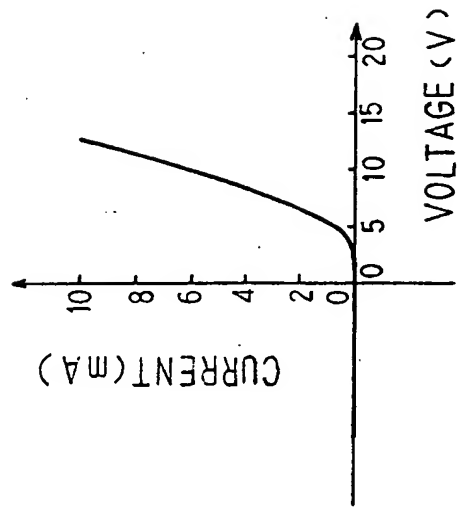


FIG. 9

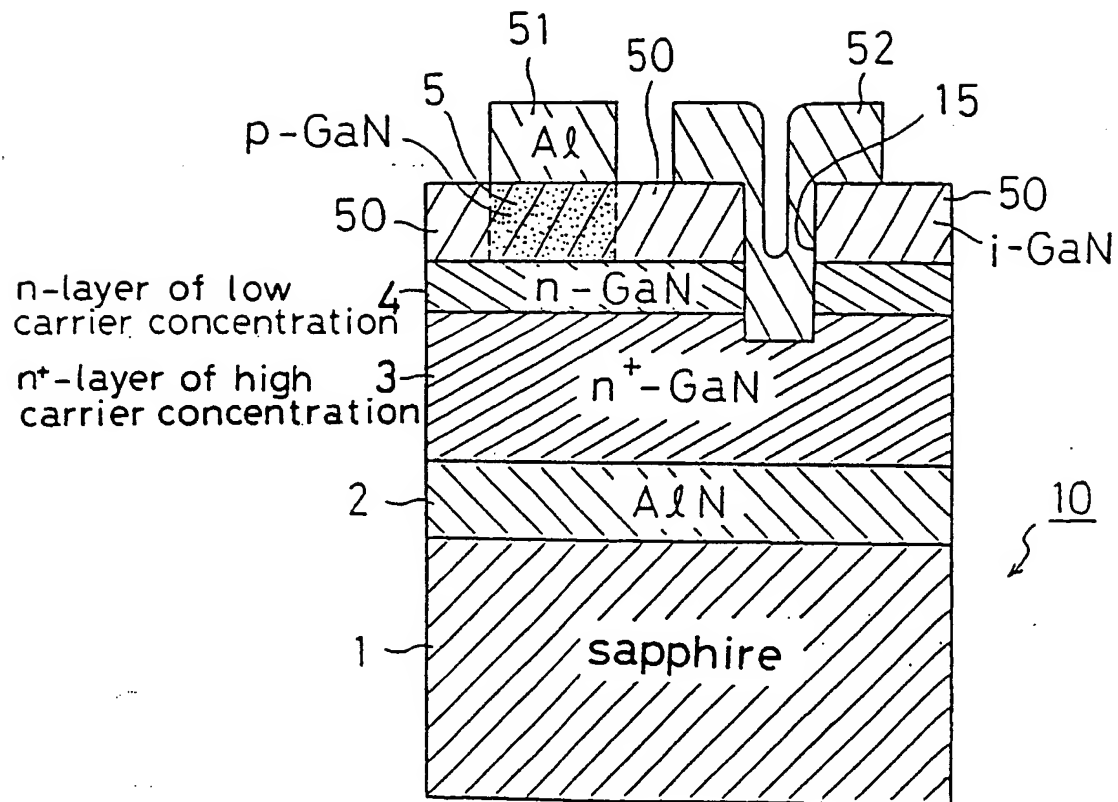


FIG. 10

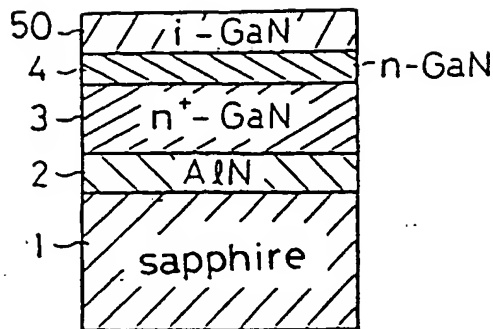


FIG. 11 A

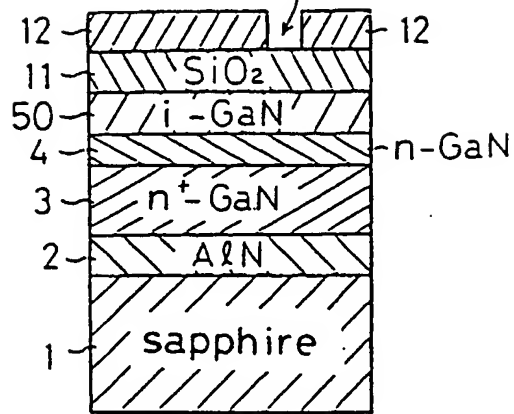


FIG. 12

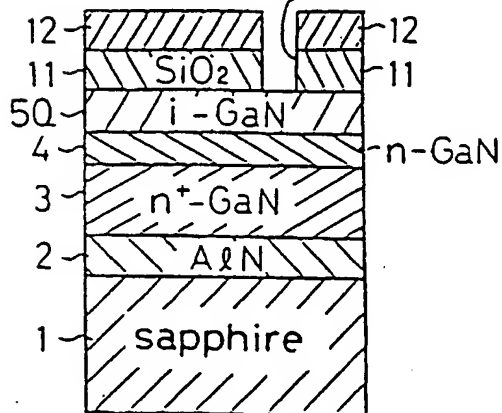


FIG. 13

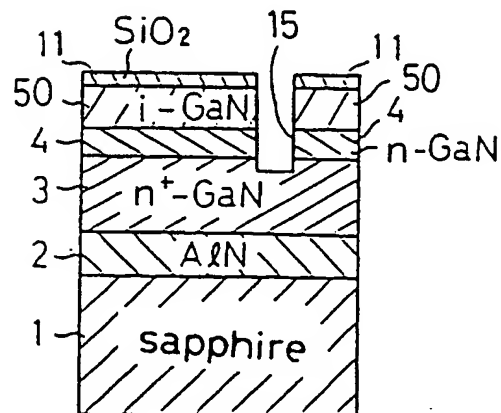


FIG. 14

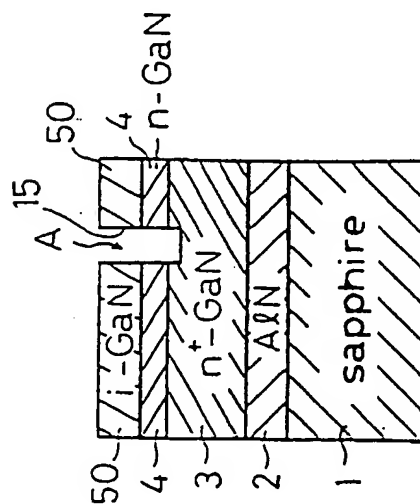


FIG. 15

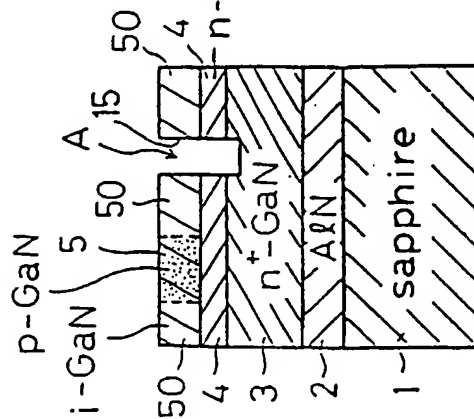


FIG. 16

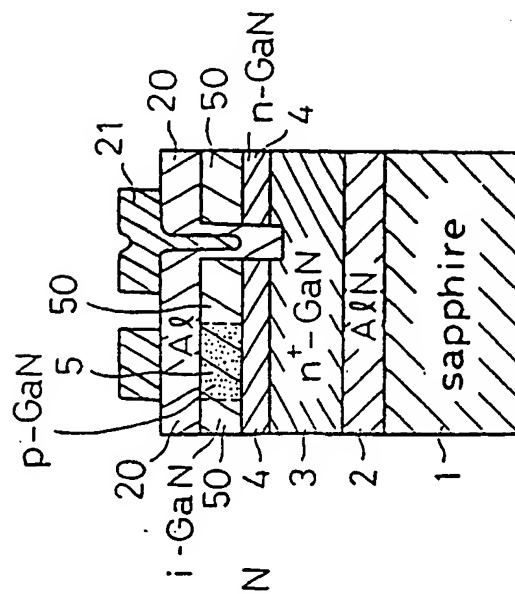


FIG. 17 A

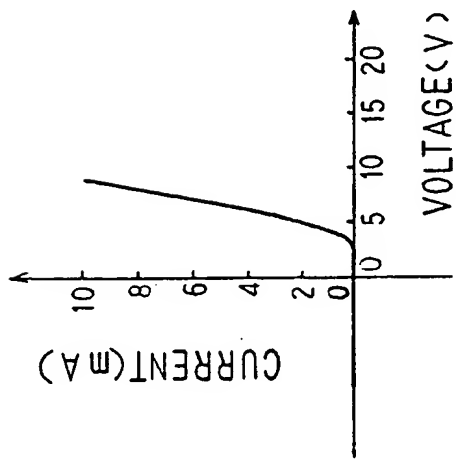


FIG. 17 B

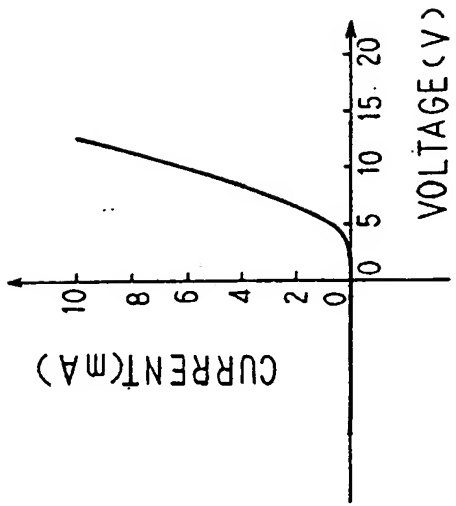
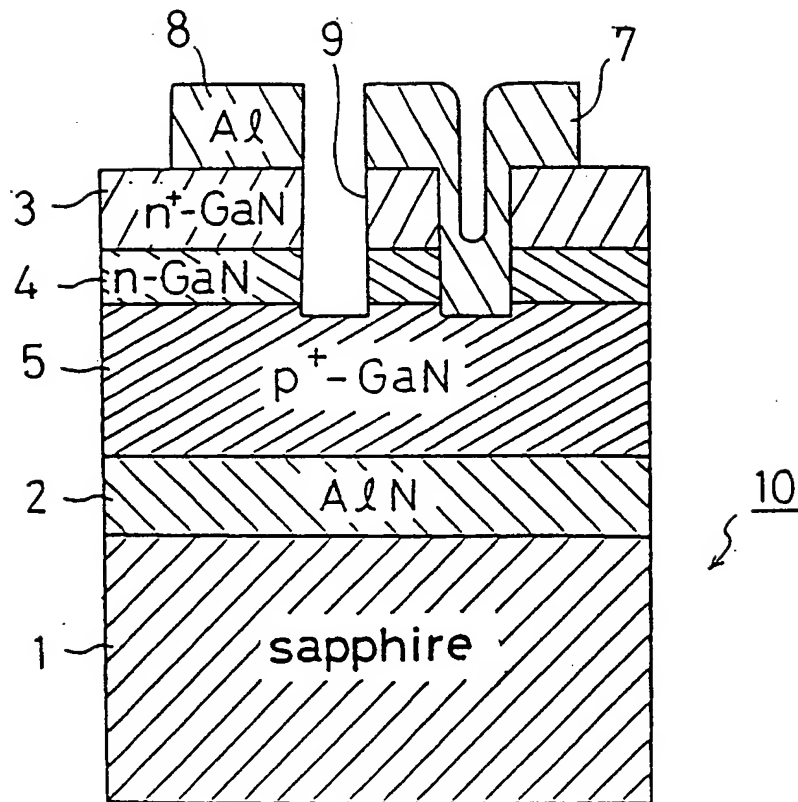




FIG. 18



(19)



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**W-8000 München 2(DE)**

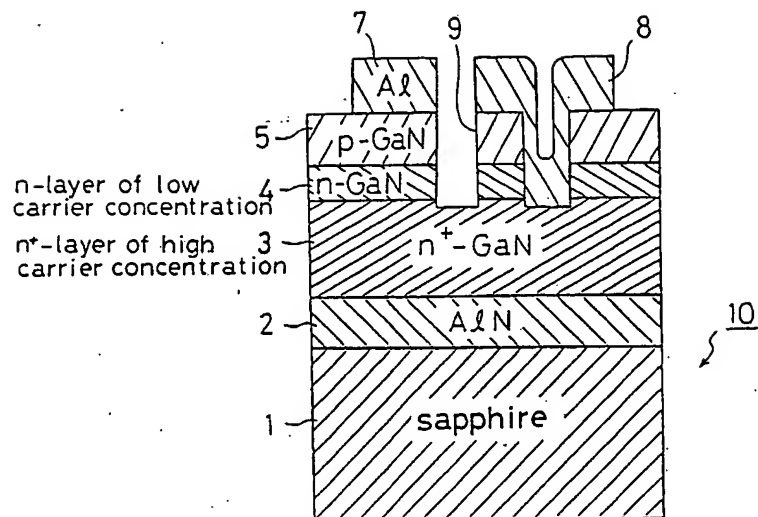
(54) **Light emitting semiconductor device using gallium nitride group compound.**

(57) There are disclosed two types of gallium nitride LED having the pn junction. An LED of gallium nitride compound semiconductor ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , where  $0 \leq x < 1$ ) comprises an n-layer; a p-layer which exhibits p-type conduction upon doping with p-type impurities and irradiation with electron rays, the p-layer joining to the n-layer; a first electrode for the n-layer so as to join to the n-layer, passing through a hole formed in the p-layer which extends from the p-layer to the n-layer; and a second electrode for the p-layer which is formed in a region which is separated by a groove formed in the p-layer so as to extend from

the upper surface of the p-layer to said n-layer. An LED comprises an n-layer; an i-layer doped with p-type impurities, the i-layer joining to the n-layer; a first electrode for said n-layer so as to join to the n-layer, passing through a hole formed in the i-layer which extends from the upper surface of the i-layer to the n-layer; a p-type part in a specific region in the i-layer which is converted into p-type conduction by irradiating with electron rays, the p-type part being formed such that said first electrode is insulated and separated by the i-layer; and a second electrode for said p-type part.

**EP 0 483 688 A3**

FIG. 1





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Application Number

EP 91 11 8253

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	JAPANESE JOURNAL OF APPLIED PHYSICS. vol. 28, no. 12, December 1989, TOKYO JP pages 2112 - 2114; H. AMANO ET AL.: 'P-Type conduction in Mg-doped GaN treated with low energy electron beam irradiation (LEEBI)' * the whole document *	1, 2, 14	H01L33/00
A	----- IDEM -----  * the whole document *	3, 7, 8, 12, 13	
X	PATENT ABSTRACTS OF JAPAN vol. 15, no. 3 (E-1019) 7 January 1991 & JP-A-2 257 679 ( UNIVERSITY NAGOYA ) 18 October 1990 * abstract *	1, 2, 14	
A	EP-A-0 277 597 (TOYODA GOSSEI CO. LTD.)  * claims *	1, 2, 12, 13	
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 263 (E-938) 7 June 1990 & JP-A-2 081 483 ( TOYODA GOSSEI CO. LTD. ) 22 March 1990 * abstract *	1, 9, 10, 11	TECHNICAL FIELDS SEARCHED (Int. Cl.5)  H01L
A	JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 137, no. 5, May 1990, MANCHESTER, NEW HAMPSHIRE US pages 1639 - 1641; H. AMANO ET AL.: 'Growth and luminescence properties of Mg-doped GaN prepared by MOVPE' * the whole document *	1, 2, 7, 12, 13	
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 200 (E-920) 24 April 1990 & JP-A-2 042 770 ( TOYODA GOSSEI CO. LTD. ) 13 February 1990 * abstract *	1, 2	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 MAY 1992	Examiner VISENTIN A.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document  T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document			



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Application Number

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	----- JOURNAL OF CRYSTAL GROWTH, vol. 98, no. 1/2, November 1989, AMSTERDAM NL pages 209 - 219; I. AKASAKI ET AL.: 'Effects of AlN buffer layer on crystallographic structure and on electrical and optical properties of GaN and Ga <sub>1-x</sub> Al <sub>x</sub> N (0<x<0.4) films grown on sapphire substrate by MOVPE'		
P,X	----- PROCEEDINGS OF THE SPIE INTERNATIONAL CONFERENCE ON PHYSICAL CONCEPTS OF MATERIALS FOR NOVEL OPTOELECTRONIC DEVICE APPLICATIONS (VOLUME SPIE 1361) 28 October 1990, AACHEN pages 138 - 149; I. AKASAKI ET AL.: 'High efficiency UV and blue emitting devices prepared by MOVPE and low energy electron beam irradiation treatment' * page 143 - page 147 *	1,2,14	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 MAY 1992	Examiner VISENTIN A.
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